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Synthetic Organic Chemicals

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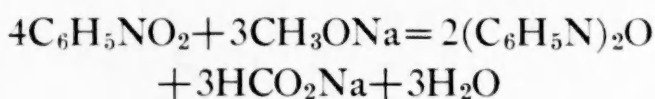
OCTOBER, 1933

No. 1

The Preparation of Azoxy Compounds

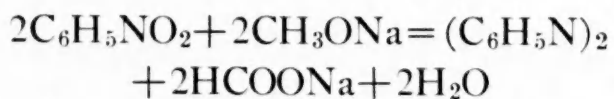
Reduction Methods

THE yellow or red crystalline substances known as azoxy derivatives were first prepared by the reaction between nitrobenzene and potassium or sodium hydroxide in alcoholic solution. Later, with nitrobenzene and sodium methylate in boiling methyl alcohol, azoxybenzene was formed in yields of 88-92% according to the equation:



A modified procedure employing sodium methylate and a solution of nitrobenzene in xylol was reported to produce a quantitative yield of the azoxy compound. If sodium benzylate is used for the reduction, azobenzene may be isolated along with benzoic acid.

The presence of ketones in the methyl alcohol is reported to be harmful to the best yields of azoxybenzene. The presence of water decreased the yield of azoxy compound obtained, and basic substances such as pyridine increased the amount of reduction, yielding both azo and azoxy compounds, the azobenzene being formed by the reaction:



In a study of the reduction of the chloronitrobenzenes it was found that

variations in the concentrations of the reacting substances, or the addition of water, caused the appearance of different products. When o-chloronitrobenzene was treated with methyl alcohol solutions of sodium methylate, variations in the concentration of sodium methylate produced o-o'-dichloroazobenzene, o-o'-dichloroazoxybenzene, and o-azoxyanisole. With sodium ethylate, o-chloroaniline and a little dichloroazobenzene or o-chloroaniline and dichloroazoxybenzene resulted.

If solutions of potassium hydroxide in aqueous methyl or ethyl alcohol be used for the reduction of o-chloronitrobenzene, o-nitroanisole or o-nitrophenetole are produced, respectively. Small amounts of acetaldehyde favor decidedly the production of the corresponding azoxy derivative. Without acetaldehyde the nitro ethers are produced.

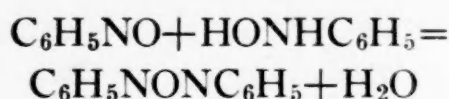
The reaction of the nitrotoluenes with alcoholates has been rather extensively studied, since with a concentrated methyl alcohol solution of potassium hydroxide, p-nitrotoluene forms dinitrodibenzyl and dinitrostilbene.

A study of the action of sodium alcoholates (or sodium derivatives of tautomeric substances) on nitrobenzene, substituted nitrobenzenes and nitrosobenzenes in anhydrous benzene solution has shown that the products are normally amines or azoxy derivatives. If sodium

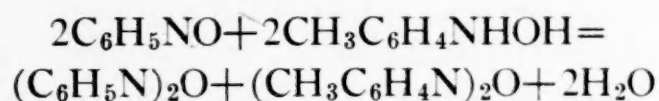
derivatives of polyhydric alcohols (ethylene glycol) be used as reducing agents, nitrobenzene forms azobenzene. If halogenated nitrobenzenes be used, the corresponding halogenated azoxybenzenes result, except when o-halogenated nitrobenzenes are used with n-propyl or n-butyl alcoholate, in which case a large amount of the corresponding α -(o-halogen anilido) propionic or α -(o-halogen anilido) butyric acid is formed.

Condensation Reactions

The condensation of nitrosobenzene with β -phenyl hydroxylamine produces azoxybenzene in quantitative yields:



Nitrosobenzene treated with p-tolyl hydroxylamine yields azoxybenzene and p-azoxytoluene:

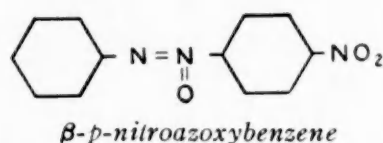
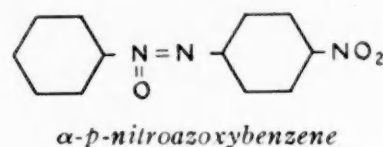


The reaction of meta-bromophenyl hydroxylamine with nitrosobenzene produces meta-dibromoazoxybenzene and azoxybenzene. The same type of reaction occurs with other hydroxylamines, for example, the benzyl derivative. A study of the velocity of reaction of substituted aryl hydroxylamines with aryl nitroso compounds indicated that when a methyl group was meta to the hydroxylamine radical, the formation of azoxy compounds was most rapid. With a methyl group para to the hydroxylamine, the reaction velocity was relatively slower, while in the ortho position the reaction rate was at the minimum. In the case of 2,6 dimethyl nitrosobenzene and 2,6 dimethyl phenyl hydroxylamine the reaction is very slow.

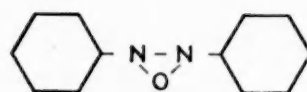
Oxidation of Azo Compounds

The preparation of azoxy derivatives by the oxidation of azobenzene with

solutions of hydrogen peroxide in acetic acid has been developed and extensively used by Angeli, with the result that isomeric substituted azoxybenzenes have been formed. This has modified extensively the earlier views on the structure of azoxy compounds. By the oxidation of p-nitroazobenzene or p-bromoazobenzene, two isomeric forms of the corresponding p-nitroazoxybenzene or p-bromoazoxybenzene may be produced. Reaction of these substituted azoxybenzenes with nitric acid and with bromine have indicated that only the β -isomers may be substituted. As a result of these investigations the isomeric forms are written as follows:

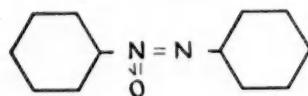


It will be noted that these structures are unsymmetrical and contain a pentavalent and trivalent nitrogen, whereas the earlier formula suggested by Kekule,



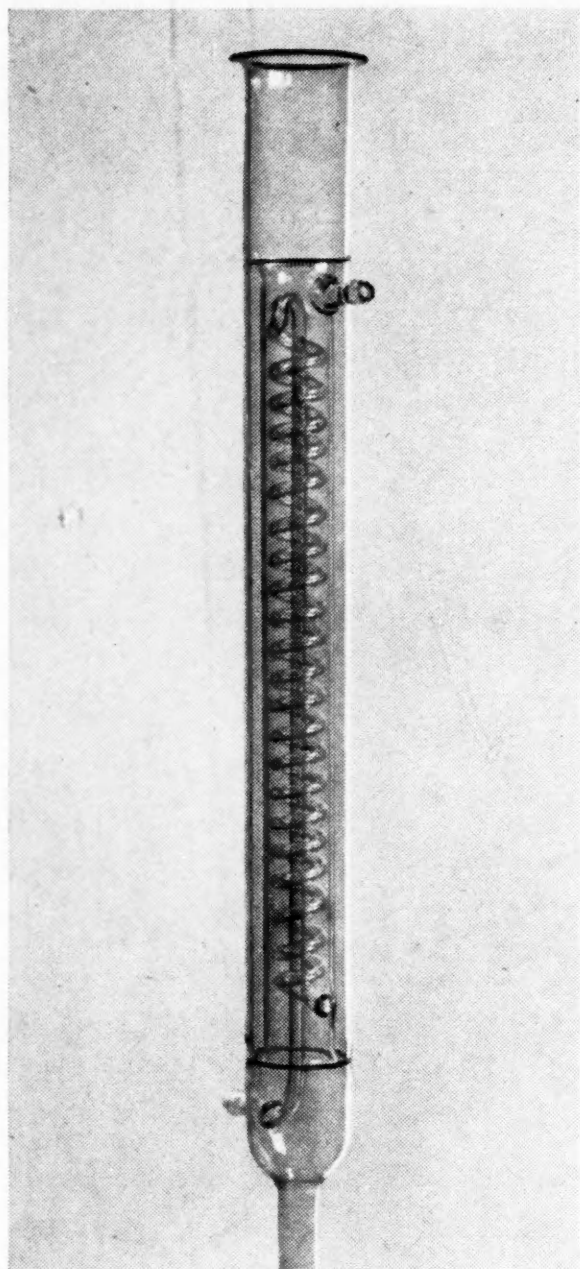
is symmetrical and contains two trivalent nitrogens. A detailed discussion of the isomerism of azoxy compounds will be found in Chem. Rev. 9, 117 (1931).

The study of parachor measurements in relation to azoxy compounds has shown that in addition to the unsymmetrical structure given above, the bond between the nitrogen and oxygen is probably the so-called "semipolar" bond or coordinate bond. Hence the structure of azoxybenzene may possibly be best represented as follows:



A Modified Liebig Condenser

The addition of a spiral cooling unit in the inner tube of the ordinary Liebig condenser improves its efficiency for several types of laboratory work. In the condenser shown above, the spiral is



made of 8 mm. tubing and has a cooling surface slightly greater than the inner wall. This additional surface thus doubles the effective condensing area without increasing the actual length.

The condenser shown was designed primarily for refluxing low-boiling liquids and for condensing liquids from escaping gases. The coils of the tubing act as a baffle and tend to prevent channeling.

Eastman Organic Chemicals as Analytical Reagents

XXX Reagents for Potassium

N-BUTYL ALCOHOL

ETHYL ACETATE

PERCHLORIC ACID

Smith and Ross, J. A. C. S. 47, 1020 (1925)

Potassium is separated from sodium and lithium by first converting the chlorides of the alkali metals to perchlorates through repeated evaporation with perchloric acid. Extraction with a hot mixture of equal parts of n-butyl alcohol and ethyl acetate dissolves the sodium and lithium salts. The insoluble potassium perchlorate is filtered off and washed with more of the mixed solvent. It is then dried in a muffle at 350° C., cooled, and weighed.

The sodium and lithium in the filtrate may be separated from each other by evaporating the ethyl acetate and precipitating the sodium as chloride with a butyl alcohol solution of hydrogen chloride. The sodium chloride is filtered off, leaving the lithium in solution.

SODIUM 5-NITRO-6-CHLOROTOLUENE-3-SULFONATE

Davies and Davies, J. CHEM. SOC. 123, 2976 (1923)

The potassium salt of the above sulfonate is about 40 times less soluble than the sodium compound and is also less soluble than potassium perchlorate or potassium chloroplatinate. The precipitate is obtained by treating any soluble potassium salt with a hot saturated solution of the reagent and allowing it to cool. Ammonium salts must be removed previously. As little as one part of potassium in 2,500 parts of water can be detected. After washing and drying at 110° C., the precipitated sulfonate contains 13.47% potassium.

New Eastman Organic Chemicals

| | | | | |
|---|------|---|--------|-----------|
| | 3495 | Acetoacet-2,5-dichloroanilide MP 93-95° | 100 g. | \$10.00 C |
| | 3535 | Amaranth | 10 g. | .50 C |
| | 3567 | n-Amyl Carbamate MP 56-57.5° | 100 g. | 8.00 C |
| | 3524 | n-Amyl Carbonate BP 130-132°/20 mm. | 500 g. | 15.00 D |
| | 3517 | n-Amyl Chlorocarbonate BP 60-62°/15 mm. | 500 g. | 15.00 D |
| | 3563 | Anthrahydroquinone Diacetate MP 261-263° dec. | 100 g. | 8.00 C |
| | 3545 | n-Butyraldoxime BP 112-114°/100 mm. | 100 g. | 4.50 C |
| | 945 | iso-Butyl iso-Butyrate BP 147-149° | 500 g. | 8.00 D |
| | 1379 | Cerotic Acid MP 80-82° | 100 g. | 15.00 C |
| | 3551 | Ceryl Alcohol MP 79-81° | 10 g. | 2.00 A |
| | 974 | Dibenzyl Ketone MP 34-35° | 100 g. | 5.00 C |
| P | 3560 | 1,2-Dichloro-n-butane (Practical) BP 121-125° | 1 kg. | 1.50 E |
| P | 3553 | 1,2-Dichloro-iso-butane (Practical) BP 107-113° | 1 kg. | 1.50 E |
| P | 3547 | 1,3-Dichloro-iso-butane (Practical) BP 135-139° | 1 kg. | 1.50 E |
| | 3454 | Diethyl-m-toluidine BP 96-97°/7 mm. | 100 g. | 9.00 C |
| | 3216 | β,β' -Diphenoxydiethyl Ether MP 64-66° | 100 g. | 10.00 C |
| | 3447 | 1-Ethyloxindole MP 95-97° | 10 g. | 3.00 A |
| | 3528 | Ethyl Undecyl Ketone MP 31-32° | 10 g. | 3.00 A |
| T | 3530 | Hexachlorophenol (Technical) MP 103-106° | 1 kg. | 2.50 E |
| P | 3556 | p-Hydroxyphenylmercuric Chloride (Practical) MP 224-225° | 100 g. | 8.00 C |
| | 3541 | Lauryl Cyanide MP 3-5° | 100 g. | 16.00 C |
| P | 3525 | Methyl Undecylenate (Practical) | 1 kg. | 9.00 E |
| | 3550 | 3-Nitrodiphenylene Oxide MP 181-183° | 100 g. | 4.50 C |
| | 3536 | Nigrosine (Water-soluble) (Cert.) | 10 g. | .65 C |
| | 2095 | Nitroethane BP 111-114° | 100 g. | 15.00 C |
| T | 3491 | p-Nitrophenol Sodium Salt (Technical) | 1 kg. | 2.50 E |
| | 3464 | 3-Nitrophthalimide MP 215-216° | 100 g. | 9.00 C |
| | 3465 | Potassium 3-Nitrophthalimide | 100 g. | 12.00 C |
| | 3507 | n-Propylal BP 136.5-138.5° | 500 g. | 12.50 D |
| P | 2678 | Quinonechloroimide (Practical) MP 75-78° | 100 g. | 7.00 C |
| | 3532 | Sodium Beta-Glycerophosphate | 500 g. | 7.50 D |
| T | 3561 | Sodium Dimethyl Dithiocarbamate (Technical) | 1 kg. | 5.00 E |
| T | 3570 | Sodium Di-n-butyl Dithiocarbamate (Technical) | 500 g. | 5.00 D |
| T | 3566 | Sodium Dithiobenzoate (Technical) | 1 kg. | 5.00 E |
| T | 3543 | o-Sulfobenzaldehyde Sodium Salt 50% (Technical) | 500 g. | 4.50 D |
| P | 3387 | Tetraethyldiaminobenzophenone (Practical) | 500 g. | 9.50 D |
| P | 1806 | o-Tolidinedisulfonic Acid (Practical) | 1 kg. | 16.00 E |
| T | 3527 | Xylenol (Mixed) (Technical) MP 57-63° | 2 kg. | 2.80 G |